Grand Challenges in Oxides Research

Nicola Spaldin
Materials Department
UC Santa Barbara

nicola@mrl.ucsb.edu
805 893-7920

with valuable input from:
Leon Balents (UCSB), Jeroen van den Brink (U Leiden), Jaques Chakalian (U Arkansas), Matthew Fisher (UCSB), Michael Fisher (U Maryland), Supratik Guha (IBM), Werner Hanke (U Wurzburg), Daniel Khomskii (U Koln), R. Ramesh (UC Berkeley), Art Ramirez (Bell Labs.), Richard Scalettar (UC Davis), Darrell Schlom (Penn State), Jim Speck (UCSB), Susanne Stemmer (UCSB), Chris van de Walle (UCSB)

the CMMP 2010 and BESAC Grand Challenges reports
The simplest complex oxide: $\text{SrTiO}_3$


*Atomic-scale imaging of nano-engineered oxygen vacancy profiles in $\text{SrTiO}_3$, D. Muller et al., Nature 430, 657 (2004)*
Grand challenge

To achieve the same level of synthetic control and fundamental understanding as is currently attained in semiconductors and simple metals
Why oxides?

- Abundance!
- Non-toxic
- Polarizability *just right*
- Nitrides too covalent
- Fluorides too ionic
- Diverse chemistries, structures and dimensionalities
- Strong correlations! Behavior of one electron explicitly influences the others
Strong correlations

**a wide range of couplings:**  
electron-lattice  
electron-spin(-lattice)  
spin-orbital

**potential technological relevance:**  
high-k dielectrics  
ferroelectricity  
high-\( T_c \) superconductivity  
large thermopower  
multiferroism  
magnetoelectricity  
magnetoresistance  
spintronics  
piezomagnetism  
magnetic frustration

---

**Spin/orbital/lattice couplings have similar energy scales**  
small energy changes (surfaces, interfaces, defects, external perturbations) can shift balance between competing large energy interactions and vastly alter ground state  

---

**TUNABILITY!**
Strong correlations

Spin/orbital/lattice couplings with similar energy scales
small energy changes (surfaces, interfaces, defects, external perturbations) can shift balance between competing large energy interactions and vastly alter ground state

TUNABILITY!

Comparison with conventional semiconductors

Conventional semiconductors

Physics:
- large overlap of s/p orbitals gives extended wavefunctions
- no intrinsic magnetism or other correlations

Technology:
- **Quality**: high! can be fabricated into complex structures
- **Understanding**: Semiconductor modeling is straightforward
- **Tunability**: control charge with modest doping/ E fields
Comparison with conventional semiconductors

**Conventional semiconductors**

**Physics:**
- large overlap of s/p orbitals gives extended wavefunctions
- no intrinsic magnetism or other correlations

**Technology:**
- **Quality:** high! can be fabricated into complex structures
- **Understanding:** Semiconductor modeling is straightforward
- **Tunability:** control charge with modest doping/ E fields

**Complex oxides**

**Physics:**
- localization of 3d/2p orbitals gives strong Coulomb interactions
- diverse magnetic and other strong correlations

**Technology:**
- **Quality:** materials chemistry challenging; fabrication less developed
- **Understanding:** strong correlations challenging to theoretical tools
- **Tunability:** high! due to competing ordered states
### Conventional semiconductors

**Physics:**
- large overlap of s/p orbitals gives extended wavefunctions
- no intrinsic magnetism or other correlations  

**Technology:**
- **Quality:** high! can be fabricated into complex structures
- **Understanding:** Semiconductor modeling is straightforward
- **Tunability:** control charge with modest doping/ E fields

### Complex oxides

**Physics:**
- localization of 3d/2p orbitals gives strong Coulomb interactions
- diverse magnetic and other correlations

**Technology:**
- **Quality:** materials chemistry challenging; fabrication less developed
- **Understanding:** strong correlations challenging to theoretical tools
- **Tunability:** high! due to competing ordered states

vastly richer physics suggests entirely new functionalities provided *Oxides Grand Challenge* can be met:

| To achieve the same level of synthetic control and fundamental understanding as is currently attained in semiconductors and simple metals |
Why now?

Growth/synthesis:
Quantum Hall Effect at ZnO/(Zn,Mg)O interface $\rightarrow$ high quality samples


Understanding:
- improved experimental probes (ARPES, STM, SNS)
- theory/computation able to address intricacies numerically
Existing technology need: High-k oxide-based CMOS technology:

Gate leakage power growing exponentially as gate length is reduced

C = k/d; Need a high-k replacement for SiO₂ to continue CMOS scaling

Fully processed transistor with high-k/metal gate:

IBM high-k product: Expected 2008

This is the first major technology application for nanoscale metal oxides in electronics
To achieve the same level of synthetic control and fundamental understanding as is currently attained in semiconductors and simple metals

Sub-challenges:
- growth/synthesis
- theory/computation

Two most exciting current/developing areas:
- oxide-oxide interfaces
- multi-functional oxides
A “mini seminar” on theory/experiment interplay in multiferroics
Challenge: Synthesis

BiFeO$_3$

grown from B$_2$O$_3$/Bi$_2$O$_3$/Fe$_2$O$_3$ flux

Bi$_2$Fe$_4$O$_9$ more stable
Fe$_3$O$_4$ decomposition product!
Single crystal growth

need for bulk single crystal growth
best (sometimes essential) for accurate characterization (dielectric measurements, neutrons, x-rays)
required as substrates for homoepitaxy
new materials: ternaries and quaternaries

dedicated equipment and operators
many oxides melt at high temperatures (> 1500°C)
some require toxic fluxes (e.g. Bi)
some require high pressure (many Bi-based multiferroics)

New materials synthesis and crystal growth study
Paul Peercy and Art Ramirez, tomorrow am
Thin film growth

Films offer additional capabilities
- stabilizing phases which are not the bulk thermodynamic ground state
- chemical control through layer-by-layer deposition
- multilayers with precisely engineered interfaces
- modifying properties with strain
- required for devices

Need for improved film quality
- complex oxide films are often far from stoichiometry
- current composition control limits around 1%
- oxide MBE (molecular beam epitaxy) versus PLD (pulsed laser deposition)

![Graph showing Sr/Ti Ratio vs. Sr Content with data points for MBE, PLD, and Sputtering methods]
Challenges in theoretical description of complex oxides

Strong correlations lead to many-body effects
traditionally (successfully) described with model Hamiltonians

Complete description of structure and chemistry essential
traditionally (successfully) performed within a mean-field treatment

Need techniques that include chemistry, structure and many-body interactions on an equal footing
Incorporating many-body effects in “structure and chemistry” methods

Density Functional Theory

Interacting many-electron system

Kohn-Sham Equations

\[ \{ T + V_{ei}(r) + V_H(r) + V_{xc}(r) \} \phi_i(r) = \varepsilon_i \phi_i(r) \]

System of non-interacting electrons

Allows us in principle to calculate ground state properties:

charge densities and energies, crystal structures, electronic band structures, magnetic ordering, phonon frequencies, ferroelectric polarizations, dielectric response, piezoelectric coefficients...
Incorporating many-body effects in “structure and chemistry” methods

BUT...

\[ \{T+V_{ei}(r)+V_{H}(r)+V_{xc}(r)\} \phi_i(r) = \varepsilon_i \phi_i(r) \]

\( V_{xc}(r) \) is approximated

“Standard” local density approximation (LDA) treats as a homogeneous electron gas

Beyond-LDA methods:

- LDA+U attempts to incorporate Coulomb repulsions (U)
- Self-interaction corrections (SIC) attempt to account for spurious self-XC
- LDA+DMFT (dynamical mean field theory)

Downfolding:

Extract essential interaction parameters from LDA and construct a model

Needs:

- Greater supercomputing capacity in central facilities
- A system for supporting the maintenance of public codes
Other challenges in DFT-based theory: Finite Electric Fields

Two difficulties:

1) Infinite crystal in uniform external field does not have a ground state:

2) Potential with electric field is non-periodic

Solved (very recently) using tricks:


Outline

Sub-challenges:
- growth/synthesis
- theory/computation

Two most exciting current/developing areas:
- oxide-oxide interfaces
- multi-functional oxides
  A “mini seminar” on theory/experiment interplay in multiferroics
Oxide-oxide interfaces

“The interface is the device”
Herbert Kroemer, Nobel lecture, Dec 8 2000
Oxide-oxide interfaces

“The interface is the device”
Herbert Kroemer,
Nobel lecture, Dec 8 2000
Example of new functionality at oxide-oxide interfaces

Electron microscopy image of LaTiO$_3$ layers (bright) spaced by SrTiO$_3$ layers

Example of new functionality at oxide-oxide interfaces

Electron microscopy image of LaTiO$_3$ layers (bright) spaced by SrTiO$_3$ layers

LaTiO$_3$

$\text{Ti}^{3+} \ (3d)^1$

Mott insulator

SrTiO$_3$

$\text{Ti}^{4+} \ (3d)^0$

Band insulator

Example of new functionality at oxide-oxide interfaces

Electron microscopy image of LaTiO₃ layers (bright) spaced by SrTiO₃ layers

LaTiO₃
Ti³⁺ (3d)¹
Mott insulator

SrTiO₃
Ti⁴⁺ (3d)⁰
Band insulator

The conflicted d electron spreads out...


(magnetic) metal at the interface!
Incompatible magnetism at oxide-oxide interfaces

“A-type” antiferromagnet
e.g. LaMnO$_3$

“G-type” antiferromagnet
e.g. LaFeO$_3$
Frustrated magnetism at oxide-oxide interfaces

“A-type” antiferromagnet
e.g. LaMnO$_3$

“G-type” antiferromagnet
e.g. LaFeO$_3$

Possibilities: frustrated magnetism, change in orbital ordering at interface (propagation into bulk?), charge transfer/change in oxidation states, ???

HUGE POTENTIAL!
Tremendous progress in synthesis, characterization and understanding of novel complex oxides

Many new (unanticipated) physical phenomena emerging in single phases and at interfaces

Demand for oxides in existing technological applications
  - high-k dielectrics
  - oxides as semiconductors
  - dissipationless wires from high (room) temperature superconductors

Possibility for entirely new device paradigms
  - strong correlations
  - multifunctionality

Plan for coordinating fundamental discoveries with new technologies?